"STUDIES ON SOLUTE- SOLVENT INTERACTIONS IN IONIC LIQUID SYSTEMS"

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Synopsis of Thesis

Title

Studies on Solute-Solvent interactions in ionic liquid systems

Introduction:

Electrolyte solutions historically set themselves apart from ordinary solutions in the study of mixtures. For many years, very few standard texts on solutions (one by Hildebrand and Scott) were written for nonelectrolytes. However, it was not until the 1960s and 1970s when liquid state theories had well developed that a common approach to electrolyte and non-electrolyte solutions became possible.

This fact be speaks the difficulty in treating electrically charged species located in a dielectric continuum of the solvent. The common basis is the statistical molecular distribution functions (a historical review, given in Falkenhagen 'Electrolytes'), and a relation (Poisson Boltzmann equation), to correlate the charge distribution in ion-atmosphere, to the potential at a central ion which happens to be the focus of the attention, for the Physio-chemical activity. One of the earliest efforts in describing dissolved salts was undertaken by Debye - Huckel .This is the Basic model even today; in spite of several attributed lapses in it. A viable model is expected to provide a sensible explanation to several observations made in several angles for the determinations of several Physio- chemical parameters.

In this thesis, the author attempted to account for some of the lapses in the theoretical models that became evident by 1990's and later. This forms the backbone of the work reported in this thesis. The author attempted to obtain experimental data in his dielectric studies on aqueous Sulphates (Cu, Ni, Mn and Co),Chlorides (Cu, Ni, Mn and Co) and Nitrates (Cu, Co, Cd and Cr) of transition metals at 298K with latest Operational amplifier technique, that was designed and fabricated by the author at Godavari Institute of Engineering and Technology, Rajahmundry, A.P. INDIA. This data is applied to calculate thermodynamic parameters like Activity coefficient, Osmotic coefficient and Excess Gibbs energy for these transition metals using well known Pitzer model, Bromley model and Lu and Maurer model. The author in an attempt to apply Ultrasonic, Densimetric and Electromagnetic tools to validate the findings of Chandrika

Akilan. She has specifically chosen Copper Sulphate and incorporate the influence of dielectric constant, along with solute - solvent interactions, and solvent to solvent interactions on the short and long range interactions , in the binary solvent mixtures of water and ethylene glycol. As many as eleven compositions of this mixed solvent system, with the electrolyte dissolved in each of the compositions, from concentration range of the electrolyte dissolved from 0.1M to 0.6M, are used in our experimentation. The author studied these systems at five temperatures i.e., 298K, 303K, 308K, 313K, 318K, with the Antonpaar setup. Interestingly the result of the study revealed several discrete characteristic evidences of the Nobel Prize winning Eigen and Tomm Ion Pairing Mechanism (ETIPM). The acoustic data obtained was interpreted in terms of several theories of structure making and breaking, Complexation, polar interactions involving ions and the solvent molecules, cluster formation mechanisms, etc. There is a very good agreement between the reported results of the author and similar findings quoted from the literature at the appropriate places.

Other than introduction, the essential chapters of the thesis are organised as per the plan given below.

Chapter 1: Literature survey:

This chapter gives a detailed survey of the Reviews and Ph.D. thesis of Scientists of repute belonging to different universities, around the globe, related to: Thermodynamic, Dielectric, Ultrasonic, Densimetric, and Electromagnetic studies of ionic liquid systems, referred by the author in connection with the work reported in the thesis. Important Books referred during the progress of the work, research publications in Journals of esteem, several review articles, and International and National Conference reports and Proceedings are detailed in this chapter.

This chapter essentially is classified into three parts. In the first part a detailed survey of the Ph.D., thesis of scientists is presented. In the second part, work reported in relevant to the author's work is outlined from standard text books of reputed authors. In the Third part, important information used by the author during the progress of the work, is detailed from several review articles, published research papers of scientists, International and National Conference reports.

Chapter 2: Theoretical Models:

Several details of the models used in our work are presented separately in this chapter on 'Theoretical Models' of this thesis. Much earlier to our attempts, the Debye-Huckel model was extended by Fuoss and Accascina, Pitts, Fuoss and Onsager, Fuoss and Hsia, Kremp et.al, Kraeft et.al, and Sandig and Kraeft. Recent models of electrolyte systems by several authors were cited and a comparison between them is given. Models proposed by Pitzer, Bromley, Lu and Maurer are chosen for the application of the determined dielectric and other data.

The Debye- Huckel model that forms the backbone for the development of the models even today, was presented in a reasonable depth. All the assumptions about the Ion Atmosphere and its characteristics were given in a reasonable detail. Characteristics of the charge distribution, choice of the distribution function, and the electro- phoretic and relaxation mechanisms in the dielectric continuum of the solvent were discussed. The basic approximations made by Debye - Huckel, about the application of Poisson-Boltzmann Distribution Equation, were detailed.

The theoretical equations were presented in a reasonable detail. The equations for the Activity coefficient and Osmotic coefficient from the D-H model were given and several inconsistencies in these equations which require a correction were detailed.

The propositions of the Pitzer model, chosen to be the recent improvement over the D-H model, and a brief sketch of the historical perspective of the development of the model are presented. Concepts in the application of the virial theorem, and the involved inaccuracies were listed. The possible discrepancies in the interpretation of the experimental results, when this model is applied are cited. The Equations for Activity, Osmotic Coefficients and important concepts involved in the Pitzer's model are given. An outline of the Bromley's model is presented, along with the essential equations. The possible implications of the approximations are critically analysed, in the perspective of the application of our data .The essentials of the Lu and Maurer model and its extensions are presented. Its application in the evaluation of the excess Gibbs energy data is detailed. The essentials of the Glueckauff's model for the estimation of the depression in the dielectric constant are given. The limitations of the approximations are discussed. A few of the very recent models on which the author intends to extend his studies in

future are presented in a nut shell. All the related parameters used in the work are suitably explained, to make the thesis self-contained.

Chapter 3: Experimental Techniques:

This chapter describes the Experimental Techniques, the details of the equipment used by the author, their accuracies, fundamental principles of their functioning, and several other details.

The techniques described are: (1) Operational amplifier based technique for dielectric constant determination of chosen aqueous Sulphates, Chlorides, Nitrates at 298Kalong with precise temperature variation studies, designed and fabricated by the author. This temperature variation of dielectric constants of Methanol, Benzene, Nitrobenzene and water, are obtained using.

AN 685 temperature sensor with above technique. (2) The Austrian made Antonpaar experimental setup, DSA-5000M used for the very accurate determination of Ultrasonic velocity, density, and Antonpaar's Abbemate Refractometer for evaluation of Refractive index of the electrolyte solution of Copper Sulphate in binary solvent mixture of Ethylene glycol and water in eleven compositions and six concentrations of the electrolyte at different temperatures was presented in detail. A very accurate digital Micro balance, Sartorius CPA -225D, is used to determine the mass of the electrolyte. The equipment is very sophisticated, and can automatically change the temperature in chosen steps. The data is obtainable directly from the setup in the form of print out, in any assigned format. We require only 5 ml of the solution for the determination of the data, for a given set of temperatures that can be prefixed in a software programme.

Chapter 4: Results and Discussion:

This chapter presents the outcome of the author's evaluations in the form of tables, plots, with necessary interpretations. As far as possible Mat Lab programmes are used in calculations, to avoid human errors. The entire used Mat lab Programmes are listed at the end of the thesis in Appendix-B. Origin-6 version software is used for the purpose of drawing the plots. The

dielectric data obtained experimentally is shown along with the theoretically evaluated component as ordinates.

The data presented in the chapter broadly consists of five parts:

Part: 1. Dielectric studies: In this part, the deviations in experimentally calculated dielectric data are explained on the basis of ion pair formation mechanism of chosen aqueous electrolytes, sulphates, chlorides and nitrates of transition metals evaluated experimentally with latest operational amplifier technique designed by the author. This data is in good agreement with the data obtained from literature.

Part: 2.Thermodynamic studies: In this part, the outcome in the theoretically evaluated data of activity and osmotic coefficients, excess Gibbs energy of chosen aqueous electrolytes from Pitzer model, Bromley model and Lu and Maurer model are discussed on the basis of formation of three types of ion pairs namely solvent separated, solvent shared and contact ion types. Several concepts regarding theories of association, solute solvent interactions, and structural properties using standard theories like cluster making and cluster breaking, and common ion effect, polar interaction, hydrophilic and hydrophobic interaction, and micellar formation etc., found in the literature, were invoked to explain results .

Part: 3. Ultrasonic studies: In this part, the experimental results of ultrasonic velocity U and density ρ obtained from Anton paar equipment are discussed with the help of graphs for chosen copper sulphate in the mixture of water and Ethylene glycol as solvent. From this data,other calculated parameters like Adiabatic Compressibility β; Acoustic impedance Z, Inter molecular free length L_f, Relative Association of the solution R_A , Surface Tension σ, were discussed.

Part: 4. Densimetric study: The apparent and partial molal volumes of electrolyte solutions have proved a very important tool in elucidating the structural interactions i.e. ion-ion, ion-solvent and solute-solvent interactions occurring in solution. In this part, these structural interactions were discussed for two parameters, apparent molal volume ϕ_V and apparent molal compressibility ϕ_K.

Part: 5. Refractive index studies: In this part, the Refractive index data of ternary solution of copper sulphate in Ethylene glycol and water in eleven compositions and six concentrations of

the electrolyte at different temperatures, obtained from Antonpaar's Abbemate refractometer, is used to analyse solute-solvent and solvent-solvent interactions.

Chapter 5: Conclusions and scope of future work:

As per Bob Eisenberg (beisenbe@rush.edu)the ionic liquids are essential liquids of life and are not ideal solutions. Especially chemically specific properties come from interactions in ionic solutions which arise due to Force Fields (http://arxiv.org/ as q-bio/0506016v2) ,that are not dealt with comprehensively so far in any model. These fields show the dependence of the dielectric constant on 1. Temperature, 2. Short Range interactions, 3. Long Range interactions, 4. Ion- Solvent and 5. Solvent- Solvent interactions (for the case of Binary Solvent Systems). It is imminent that such a dielectric model should be impregnated into the basic Debye- Huckel theory, since the "κ", parameter (of the Ionic atmosphere around the central ion) appears at all the prominent places in the theories of ionic interactions, (e.g., the Basic Bjerrum's hypothesis, and equations used by Barthel, Buchner et.al,, Hefter & Wang and Anderko et.al,) and other mechanisms developed later, in the dielectric relaxation and other related studies. Even the very recent models are attempting several other approaches, and hence are unable to be comprehensive. This aspect is being pursued at present in our group led by Brahmajirao et.al, and we intend to publish the outcomes very shortly. Almost all the observations of Chandrika Akilan (2008) are confirmed in these studies on Activity Coefficients and other thermodynamic parameters. This aspect is clearly explained in the published papers of the author, cited in the list of his publications that appeared in reputed journals and presented on the platforms of Conferences of Repute.

The studies with the experimental techniques produced interesting results. Most of them are not only in tune to the developing theories, but also provided several leads into the propositions of all these theories. These leads are predictable from analysis of the results, and would be used to plan for the future work.